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SYNTHESIS AND CHARACTERIZATION OF RADIATION CURABLE POLYURETHANES

CONTAINING PENDANT ACRYLATE GROUPS

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ABSTRACT

A series of radiation sensitive and relatively high molecular weight polytetramethyleneadipate polyurethanes containing pendant acrylate functionality was synthesized. These radiation curable materials possess good mechanical properties and behave like common thermoplastic elastomers prior to chemical crosslinking which further enhances their strength and insolublizes them. Both the precursor and the cured materials were characterized by stress-strain, differential scanning calorimetry, and dynamic mechanical testing. It was found that the polytetramethylene adipate soft segments with molecular weight of 2000 or higher were crystallizable in the crosslinked network. The soft segment molecular weight and the diisocyanate type were found to be important in determining the tensile and thermal properties of these materials. The crosslinking process was found to depress crystallization of the soft segments and to improve tensile properties. Increasing the soft segment molecular weight resulted in an increased elongation at break but a decreaed ultimate stress for both the precursor linear polymers and the crosskinked materials.

INTRODUCTION

Polyurethane-acrylate radiation curable materials have been the subject of much recent interest [1-3]. Most of the materials previously described were liquids in the oligomer state which were subsequently crosslinked using visible, ultraviolet, or electron beam radiation. The low viscosity liquid

oligomers possessed excellent processability while the cured solid polymers had reasonable mechanical strength and good thermal stability due to their crosslinked nature. The radiation polymerization and crosslinking process has many advantages compared to traditional solvent evaporation coating technologies as applied to high polymer materials. Since the liquid oligomers are 100% reactive, no solvent evaporation or recovery equipment is needed and environmental polution is minimized. The radiation curing process also does not consume as much energy as solvent coating.

The major components of radiation curable systems are the reactive oligomers, reactive diluents, and the photoinitiator. Other additives can include non-reactive modifiers, pigments, and plasticizers, etc. The most important component in these systems in determining the mechanical properties is the reactive oligomer. Therefore, the molecular design of the reactive oligomer has been a major concern in this developing technology.

Although many liquid oligomers have been developed, little attention was given to reactive polymeric precursors which possess good initial mechanical properties which can then be further reacted to form strong and insoluble materials by high intensity radiation. In this case, the reactive polymer must not only have a high enough molecular weight to provide initial strength but must also contain a relatively high concentration of the functional groups which may be reacted during the irradiation process.

Polymers containing acrylate or methacrylate pendant groups are candidates for radiation sensitive solid polymers since the acrylate groups may undergo crosslinking reaction under suitable conditions. Acrylated urethane comb-like materials, can potentially combine the high abrasion resistance, toughness, tear strength, and good low temperature properties of polyurethanes with good optical properties and weatherability of the polyacrylates. In this urethane acrylate system, the polyurethane backbone may contain polyether or polyester soft segments, diisocyanate/short chain diol hard segment, and acrylate pendent groups which are highly responsive to radiation in the presence of photoinitiator. The microphase separated morphology of the polyurethane provides initial mechanical strength while further crosslinking can enhance mechanical properties especially at higher temperatures.

Oraby and Walsh studied the mechanical properties of electron beam cured acrylated polyester urethanes based on toluene diisocyanate(TDI) and hydroxyethyl-methacrylate(HEMA) oligomers of varying oligomer structure, monomer content, and extent of crosslinking [4-5]. It was shown from stress-strain and thermal property data that increasing the molecular weight of the urethane acrylate oligomer from 1000 to 4000 resulted in a decrease in the stress at break, Young's modulus and glass transition temperature of the polyester segments, while sample elongation increased. Based on dynamic mechanical and microscopic studies, Wadhwa and Walsh concluded that these polyurethane acrylates have a one phase morphology in which hard and soft segments are homogeneously mixed [6]. Park, et. al.,

investigated the effects of crosslink density on the morphology of acrylated polyurethanes with crystallizable polyester soft segments. Increased crosslink density reduced the degree of crystallinity and improved tensile strength [7-8]. In a series of publications from this laboratory [3,9-10], the properties of various polyether and polyester urethane acrylate radiation curable materials were reported. The effects of polyether and polyester molecular weight, diisocyanate and acrylate type, and reactive diluent content were systematically studied. It was concluded that these materials generally possess a two phase microstructure, a polyol rich phase, and an acrylate-diisocyanate rich phase, although the degree of phase mixing is larger than in ordinary polyurethanes. It was also found that the degree of phase mixing were influenced by the isocyanate and acrylate components. Toluene diisocyanate - hydroxyethylmethacrylate (TDI-HEMA) or isophorone diisocyanate - hydroxylethylmethacrylate (IPDI-HEMA) based materials possessed higher hard domain fractions, Young's modulus, and stress at break compared with isocyanatoethyl methacrylate (IEM) based materials. Addition of reactive monomer (reactive diluent) reduces the viscosity of the oligomer and improves processibility. Increasing the reactive diluent content had the effect of increasing both the degree of phase separation and the acrylate-urethane-reactive diluent hard phase volume fraction. It was found that higher reactive diluent contents led to increasing dynamic and tensile moduli and increasing tensile strength.

The physical properties of polyurethane acrylates based on liquid oli-
gomers and reactive diluents have been reported in literature [1-8], and
their structure property relationships have been studied extensively in
this laboratory [3,9-11]. The synthesis of solid radiation sensitive
polyurethanes and characterization of their physical properties in both the
precursor and cured state have not been reported.

In this investigation, radiation sensitive comb like acrylated
polyester polyurethanes based on polytetramethylene adipate (PTMA) soft
segments, 4,4'-methylene diphenylene diisocyanate (MDI) or isophorone
diisocyanate (IPDI), and glycerine or dihydroxy amino propane (DAHP) hard
segments were studied. The synthesis reactions take the advantage of the
lower reactivity of the secondary hydroxyl in the trifunctional chain
extender as the other two reactive functions are either primary hydroxyl or
amine groups. Using carefully controlled reaction conditions, it was
possible to synthesize polyurethane containing pendant secondary hydroxyl
groups along the polymer chain without gel formation [12]. Isocyanatoethyl
methacrylate (IEM) was then reacted with the secondary hydroxyl groups
thereby introducing acrylic functionality to the polymer. The acrylate
pendent groups are sensitive to radiation under favorable conditions.
These polyurethane have styrene calibrated GPC number average molecular
weights above 30,000. Unsaturated methacrylate side groups are placed at
spacings between 1500 to 5000 molecular weight along the polymer chain.
The PTMA segment molecular weight, and the diisocyanate chain extender were
varied, and their effects on the ultimate tensile properties, thermal
response, and morphology of these materials were investigated.

II. EXPERIMENTAL ASPECTS

1. Materials

A series of polytetramethylene adipate (PTMA) diol oligomer samples of molecular weight ranging from 1000 to 4000 was kindly provided by Mr. Walter T. Murphy of the B. F. Goodrich Chemical Company. Isocyanatoethylmethacrylate (IEM) was acquired from the Dow Chemical Co. HPLC grade butanone-2, N,N dimethylacetamide (DMA), and toluene were purchased from Aldrich Chemical Company, and stored over molecular sieve (type 3A, Fisher Scientific) to avoid absorbed moisture. 4,4'-methylene diphenylene diisocyanate (MDI) was obtained from Polyscience Inc. and was purified by recrystallization. Isophorone diisocyanate (IPDI) was used as received from BASF Wyandotte. Glycerine and 1,3-diamino 2-hydroxyl propane (DAHP) were purchased from Aldrich Chemical Co. Glycerine was distilled and dehydrated before using.

The comb-like polyurethane u. v. curable polymers were synthesized in a multi-step reaction scheme. The first step involved the synthesis of polyester based polyurethanes containing pendant secondary hydroxyl groups. This reaction has been reported in literature [12]. Two moles of MDI and one mole of PTMA diol were charged into a 1000 ml three neck flask containing a 2-butanone and toluene mixed solvent (1/1 vol. ratio). A magnetic stirrer was used to achieve good mixing in the reaction flask. A small amount of catalyst (0.5% triethylamine based on the weight of reactants) was added into the reaction mixture and the temperature was

raised to 80°C. A dry nitrogen purge was added to assure a moisture free environment. The reaction was kept at 80°C for 4 hr. before cooling to 45°C at which time one mole of glycerine or DAHP dissolved in N,N-dimethylacetamide was added. The chain extension reaction must be carried at the lower temperature in order to avoid crosslinking caused by reaction between secondary hydroxyl and isocyanate groups. The condensation reaction appeared to be slower at 45°C but no gelation was observed over a 24 hr. synthesis period although the viscosity of the reaction mixture increased considerably. The reaction mixture was then diluted with the butanone-toluene mixed solvent and heated to 70°C for 4 hr. to complete the chain extension reaction.

Once the linear polyester urethane with pendent hydroxyl groups was obtained, the polymer solution was again brought to 45°C. One mole of IEM dissolved in N,N dimethylacetamide (DNA) was added dropwise into the flask. Caution was exercised to avoid thermal polymerization of IEM by keeping temperatures between 45°C to 50°C. The solution was then kept at 45°C for another 24 hrs. to complete the grafting reaction.

The chemical structure of the comb-like polyurethane acrylate radiation curable materials was varied by changing the polyester diol molecular weight, the trifunctional chain extender type, and the diisocyanate type. The chemical composition of all materials synthesized for this study is listed in Table 1. GPC characterization was carried out to assure that the materials synthesized had adequate molecular weight.

The sample code contains a brief description of the structure and cure state of the material: the first two designations stand for the PTMA molecular weight and weight fraction. The third and fourth symbols describe glycerine (G) or DAHP (D) and MDI (M) or IPDI (I) were used as the chain extender or diisocyanate respectively. The last symbol indicates whether the sample was cured by u. v. radiation or not. For example, ES-1000-73-G-M-C describes a cured sample containing PTMA diol of 1000 MW, MDI and glycerine with 73 wt.% soft segment.

2. Sample Preparation

Film samples of the acrylated polyurethanes were spin cast from a polymer solution containing 0.6 wt% photoinitiator which is a 1:1 mixture of diethoxylacetophenone (DEAP) and N-methyldiethanolamine (MDEA). The films were left in a vacuum oven for one week at room temperature to remove residual solvent. All films were transparent except those made with PTMA 4000 which became opaque. Radiation curing experiments were accomplished by exposing the polymer films to a bank of u. v. lamps (max. λ = 365 nm) used as the irradiation source. The distance between sample films and the lamps was about 4 cm. In order to increase chain mobility, the temperature of the sample films during curing was kept just above polyester soft segment Tm by the use of a hot plate. Films were irradiated from one side for 40-50 minute which was more than sufficient exposure time to complete the crosslinking reaction. No experiments to determine the kinetics of the curing reaction were carried out.

Cured and uncured film samples of 200 μm thickness were used for tensile testing and differential scanning calorimetry. Thinner films of about 50 μm thickness were used for dynamic mechanical analysis.

3. Characterization Methods

a. Solvent extraction

The gel fraction of the cured samples was evaluated by extraction using various solvents for 24 hours. The insoluble gel material was dried under vacuum for about two days and weighed to determine the gel fraction.

b. *Gel permeation chromotography*

Molecular weight determination of the acrylated polyurethanes was carried out using a Waters Associate Model 501 GPC system using tetrahydrofuran as solvent and monodisperse polystyrene as molecular weight standards. Average molecular weights based on the polystyrene standards were determined from concentration-retention volume curves.

c. Stress-strain measurement

Stress-strain measurements were carried out using a table model Instron tensile testing machine at room temperature with a crosshead speed of 0.254 cm/min. 200 μm thick cured and uncured samples were stamped out using an ASTM D1708 die. The dumbell shaped samples were strained to failure and the engineering stress was calculated as the ratio of force to initial cross-sectional area.

d. Dynamic mechanical Analysis

Dynamic mechanical spectra were obtained at 110 Hz using a Toyo Rheovibron dynamic viscoelastomer Model DDV-IIC which was controlled automatically by a LSI-11/03 microprocessor. Film samples of about 2x30x0.04 mm in size were tested under a stream of moisture free ntirogen from -150 to 200°C at a heating rate of 2°C/min.

e. Differential scanning calorimetry

DSC thermograms of cured and uncured polyurethanes were obtained using a Perkin-Elmer DSC-II equipped with a thermal analysis data station and standard DSC software provided by Perkin-Elmer. Mercury and indium were used to calibrate the instrument temperature and energy settings. The data were collected from -160 to 250°C at a heating rate of 20°C/min under a helium purge. The DSC thermograms were normalized to equivalent sample weight for comparison. Glass transition temperatures and crystallization/fusion energies were determined using the DSC software.

RESULTS AND DISCUSSION

1. Synthesis and molecular characterization

The synthesis reactions have been described in the preceding sections. Scheme 1 summarizes these reactions and Table 1 shows the chemical composition of each material synthesized. It should be noted

that the chemical structure of these materials is complicated due to the trifunctional chain extender. Although the secondary hydroxyl groups have lower reactivity [12], it is impossible to eliminate the reaction of secondary hydroxyl groups with diisocyanates to form long branches. The structures shown in Scheme 1 are suggested to be the major components in the system. The molecular weight distribution of these polymers is inherently broader than their linear counterparts. GPC data are listed in Table 1. These materials have GPC average molecular weights not lower than 30,000 have adequate physical properties for characterization in the uncured state [13-14].

2. Crosslinking processes

Since the uncured materials are solids at room temperature, the polymer chain motions are depressed compared with radiation sensitive oligomeric liquids. As a result, the solid acrylated urethanes u. v. curing reaction is less efficient. In this study, all samples were heated to a temperature above the melting point of PTMA segments to promote chain backbone motion and photopolymerization of acrylate groups attached to the polymer. The curing time to obtain a 95% gel fraction was much longer than that required for liquid oligomers studied previously [3,9-11] . It was found that the curing time was almost independent of soft segment molecular weight when the curing temperature was kept above PTMA T_m. Considering that the samples prepared with 1000 MW PTMA segments have a higher acrylate concentration than samples based on PTMA 4000, the effect of the higher acrylate concentration might be off-

set by the lower segmental mobility caused by the shorter chain length
existing between crosslinks at an intermediate stage of curing. No
attempt was made to study the rate of curing of these samples quan-
titatively.

3. Thermal properties

Figures 1 to 4 show the DSC thermograms of the radiation sensitive
polyester urethane acrylate materials in their initial and cured
states. Table 2 summarizes the thermal transition data derived from the
DSC analysis. The PTMA segment glass transition temperature varies
from -61.7°C for the pure PTMA 4000 oligomer to -5.3°C for
ES1-57-G-M-U. A DSC trace of the 4000 MW PTMA oligomer, which has a
endotherm of 20.99 Cal/gm at 51.7°C, is included in Fig. 4 for
comparison. Except those having 1000 MW PTMA segments, these materials
possess a semi-crystalline polyester phase. No hard domain glass
transition is observable from the DSC thermograms, however, as will be
discussed in next section, this does not eliminate the possibility of the
presence of a urethane acrylate phase in the system. In fact, others
have reported that several materials systems exhibiting two phase structure
in dynamic mechanical spectroscopy experiments did not exhibit two distinct
Tgs in their DSC thermograms [9].

Fig. 1 illustrates the dependence of soft segment T_g on the
polyester oligomer molecular weight. It is clear that higher soft
segment T_g appears in materials made with lower molecular weight
polyester diols. This is in agreement with the general trends of

increasing T_g with decreasing soft segment molecular weight commonly observed for polyurethane block copolymer. This trend is usually attributed to decrease in free volume and mobility due to the bonding of soft segments to rigid urethane blocks and to increased phase mixing at lower polyester molecular weight [9,16]. It is also clear that soft segment crystallinity increases as the PTMA molecular weight increases. This trend has been observed in many block copolymers containing crystallizable soft segments.

Fig. 2 shows the effect of radiation curing on the thermal properties of the amorphous acrylated polyurethanes. The curing process raises the soft segment domain T_g in both the IPDI and MDI based samples but the effect on the MDI based materials is smaller. The change of heat capacity (C_p) at the glass transition is smaller in the crosslinked samples. In the uncured state, higher polyester segment Tg of the MDI based materials implies that MDI-Glycerine-IEM hard blocks are more rigid than those of IPDI-Glycerine-IEM and may serve as better physical crosslink sites which restrict soft segment motion. The MDI based system can also have more complete microphase separation. The physical crosslinks are important to provide dimensional stability and stop cold flow in the uncured materials. Although both types of hard blocks are not crystallizable due to the pendent acrylates, the rigidity of MDI-Glycerine-IEM segments is enhanced by the aromatic structure of MDI. When the IPDI based material is chemically crosslinked, its soft segment T_g increases 17°C to a value comparable to that found in the MDI based sample as shown in Table 2. The effect of restricting segmental

motion in a three dimensional network by chemical crosslink sites is similar to that of microdomain physical crosslinks except that the former is irreversible. Very fast cooling followed by reheating has no observable effect on thermal properties of these four materials as observed by DSC.

The glass transitions of the PTMA 2000 based samples occur at slightly lower temperature than the PTMA 1000 based materials as shown in Fig. 3 and Table 2. Melting of the PTMA segments occurs at about 50°C in both the uncured and cured materials. It seems that the crosslinking process depresses crystallization and increases the amorphous portion of soft segments as indicated by the smaller melting endotherm and greater change of heat capacity at the glass transition found in ES2-73-G-M-C. In this family of samples, the crystalline polyester domains act as additional physical crosslink sites below their melting temperature, and as expected, the uncured sample with a higher crystallinity (ES2-73-G-M-U) has a higher T_g. When this sample was heated to high temperature and quenched, its crystallinity disappeared and its glass transition temperature dropped 17°C due to the release of the crystalline phase restrictions on the soft segment motion. Similar behavior is apparent in the PTMA 4000 based materials. Van Bogart et al. [16-17], have noticed soft segment crystallization in both polyether and polyester urethane block copolymers and reported that the amount of soft segment crystallinity decreased with increasing phase mixing. Lin et al. [9], however, observed no detectable soft segment crystallinity in radiation cured acrylated polyester polyurethanes based on liquid oligomers and argued that

the possibility of crystallinity was eliminated by the crosslinking. The materials investigated in this study, especially in the uncured state, have a chemical structure much closer to linear urethane block copolymers and soft segment crystallinity is expected.

It is observed in Fig. 4 that the soft segment crystallization process in the materials made with the PTMA 4000 oligomer is fast enough to be detected in the thermograms of the second heating of the quenched specimens. Higher soft segment crystallinity in these materials is indicated by higher values of normalized E_{mn} (heat of fusion per gram of soft segments in the material) as shown in the Table 2. There is about a 10°C difference in the soft segment Tg between crosslinked and precursor materials (ES4-84-G-M-C and ES4-84-G-M-U respectively). It is possible that the decrease on PTMA crystallinity is the primary reason for the lower T_g in the cured material. The samples ES4-84-D-M-U and ES4-84-D-M-C, containing the amine chain extender DAHP, have urea linkages in their structure. The urea structure has higher hydrogen bonding capability, higher rigidity, and tends to promote more complete phase separation as compared to the urethane linkage. In this study, however, no significant difference in thermal properties has been observed between the urethane and urea chain extended materials. This is partially caused by the low concentration of hard segments in all materials synthesized with the PTMA 4000 oligomer.

4. Mechanical properties

Fig. 5 to 7 show the temperature dependence of the elastic moduli and loss factors of the acrylated polyurethanes in the uncured and crosslinked states at 110 Hz. The dynamic mechanical spectra suggest that phase separation occurs in all of the materials tested. The three phases possible in the system include an amorphous polyester phase, a crystalline polyester phase, and a hard domain of composed urethane acrylate segments. Not all these phases appear in every sample; for example, no crystalline soft phase is detected in materials based on PTMA 1000. The tan δ peak at about -110°C is due to localized motions of methylene segments in PTMA [18]. The soft segment T_g appears as a peak in the loss factor at temperatures ranging from -50°C to 5°C. The sharp drop in dynamic modulus at about 54°C indicates that melting of PTMA crystals takes place at that temperature. This glass transition of urethane acrylate hard phase is indicated by a peak in the tan δ curve which occurs at about 60-100°C in some of the samples.

Ultimate tensile properties of the cured and uncured polyester urethane acrylates are summarized in Table 3. Figures 8 and 9 illustrate typical stress-strain curves for these materials. The acrylated polyurethanes of this study possess significantly improved ultimate properties compared to liquid oligomer based radiation sensitive polyurethanes reported in previous publications [3,9-11]. In fact, the stresses and strains at break observed in this study are closer to the

values of conventional linear urethane block copolymers. This is not suprising due to the structural similarities between the acrylated polyurethanes described here and their linear counterparts.

As illustrated in Fig. 5, the polyurethane acrylate materials ESl-57-G-M-U and ESl-69-G-I-U exhibit extensive phase mixing as suggested by overlapping peaks in the tan δ curve and by the gradual drop of dynamic modulus over a wide temperature range. The materials containing 1000 molecular weight polyester soft segments and amorphous urethane hard segments generally are expected to exhibit a higher degree of compatibility [9]. For these samples the soft segment glass transition temperature is found at about -40°C. The hard segment glass transitions, which are not observable in the DSC thermograms, are clearly indicated by tan δ peaks at about 60°C. Introduction of chemical crosslinks by radiation curing process raises the high temperature storage modulus as seen from these spectra. The curing process also increases both the soft and hard segment glass transition temperatures. It seems that hard domain cohesion is improved by the crosslinking reaction. MDI based ESl-57-G-M-U has higher storage modulus than IPDI based ESl-69-G-I-U. This observation is attributed to both the higher hard segment content and rigidity in the MDI based material.

Fig. 6 shows the effects of increased soft segment molecular weight on the dynamic mechanical spectra of the crosslinked materials. In accord with the DSC data, decreasing polyester molecular weight leads to a higher soft segment glass transition temperature. Decreasing polyester molecular weight also results in an increasing weight fraction of urethane acrylate segments which is indicated by the growth of the high temperature loss

factor peaks. Fig. 6 also shows that decreasing polyester molecular weight leads to an increase in the storage modulus in the high temperature rubbery region. The increase in the high temperature storage modulus is primarily due to the increase in crosslink density in the systems with shorter polyester chains. A sharp drop in storage modulus around 50°C for ES4-84-G-M-C indicates melting of the PTMA soft segments.

Dynamic mechanical spectra of materials based on PTMA 4000 are plotted in Fig. 7.   It is clear that the curing process has the effect of decreasing the soft segment T_g. This suggests that the curing process leads to a higher chain mobility in the soft domain. Fig. 7 also shows a low storage modulus for the cured materials above the transition region. This is due to the low crosslink density in these materials. Due to their low hard segment content, the uncured materials ES4-84-G-M-U and ES4-84-D-M-U rapidly soften above the polyester T_m. The DAHP chain extended material ES4-84-D-M-C may have higher degree of phase separation than the glycerine chain extended sample as suggested its distinctive low and high temperature tan δ peaks. This is attributed to the lower compatibility between the polyester soft segments and urea hard segments in the DAHP chain extended samples.

Varying the polyester soft segment molecular weight affects the tensile properties of both the acrylated polyurethanes and the crosslinked materials. As shown in Fig. 8, both ultimate stress and strain of the uncured materials increase as PTMA mlecular weight is increased from 1000 to 2000. Further increase of PTMA molecular weight causes a drop in the

strain at break but an increase in Young's modulus and stress at break. This may be attributed to the higher crystallinity found in materials with longer PTMA soft segments. Increasing polyester molecular weight from 1000 to 2000 in the cured materials results in a decrease in stress at break but increases in both Young's modulus and ultimate elongation. It is interesting to notice in Table 3 and Fig. 9 that both stress and elongation at break increase with crosslinking as the PTMA molecular weight increases to 4000 in the ES4-84-G-M-C sample. All four materials containing 4000 MW PTMA exhibit yielding points on their stress-strain curves.

The curing process has several effects on tensile properties. As indicated in Table 3, radiation curing process raises the ultimate stress of all the materials studied. For the materials having amorphous soft segments, for example, ES1-57-G-M-C and ES1-69-G-I-C, a decrease in ultimate strain is observed after curing as shown in Fig. 8. This trend is also observable in materials with low soft segment crystallinity, as in the pair of stress-strain curves of ES2-73-G-M-U and ES2-73-G-M-C in Fig. 8. When higher soft segment crystallinity appears in the material due to the presence of 4000 molecular weight PTMA, elongation at break increases after curing. This phenomena is caused by a decrease in soft segment crystallinity in the cured materials. Fig. 9 also shows that the glycerine chain extented materials have slightly enhanced tensile properties compared to the DAHP extended materials.

Fig. 8 also shows a difference in tensile properties between the MDI and IPDI based materials. A higher Young's modulus and stress at break appears in the MDI based materials due to their higher urethane acrylate

segment content and higher hard segment domain cohesion. No significant difference is found on elongation at break between the MDI and IPDI based materials.

SUMMARY

High molecular weight radiation sensitive polyurethane acrylate materials have been synthesized and effects of soft segment molecular weight, hard segment type, and radiation crosslinking have been investigated. In general, these materials exhibit physical properties similar to those of linear segmented polyurethanes rather than conventional radiation cured oligomer based polyurethane acrylates. An increase in polyester segment molecular weight leads to higher soft segment crystallinity, lower soft segment glass transition temperature, a longer polymer chain between crosslink sites in the cured materials, and a smaller hard domain content. Soft segment crystallinity results in yielding behavior being observed in the stress strain curves. Longer chain lengths between crosslinks produce higher elongations to break and lower dynamic mechanical moduli at high temperatures.

The radiation curing process increases the urethane acrylate domain rigidity and high temperature dynamic mechanical modulus and decreases the soft segment crystallinity. These factors enhance the tensile strength of the cured materials. A comparison of MDI and IPDI based samples shows that the MDI based materials possess a higher hard domain volume fraction and greater hard domain cohesion as reflected by a higher modulus above the soft segment T_g and a higher hard segment T_g.

REFERENCES

1. Schmidle, C. J., J. Coated Fabrics, 8, 10 (1978).

2. Kushner, L., and Tu, R. S., Mod. Plast., 60(4), 87 (1983).

3. Koshiba, M., Hwang, K. K. S., Foley, S. K., Yarusso, D. J., and Cooper, S. L., J. Mat. Sci., 17, 1447, (1982).

4. Oraby, W., and Walsh, W. K., J. Appl. Polym. Sci., 23, 3227 (1979).

5. Oraby, W., and Walsh, W. K., J. Appl. Polym. Sci., 23, 3243 (1979).

6. Wadhwa, L. H., and Walsh, W. K., J. ACS Org. Coat. Preprints, 42, 509, (1980).

7. Park, K., and Wilkes, G. L., ACS Org. Coat. Preprints, 41, 308 (1979).

8. Joseph, E. G., Wilkes, G. L., and Park, K., ACS Polym. Preprints, 20 520 (1979).

9. Lin, S. B., Tsay, S. Y., Speckhard, T. A., Hwang, K. K. S., Jezerc, J. J., and Cooper, S. L., Chem. Engr. Commun., 30, 251, (1984).

10. Speckhard, T. A., Hwang, K. K. S., Lin, S. B., Tsay, S. Y., Koshiba, M., Ding, Y. S., and Cooper, S. L., J. Appl. Polym. Sci., 30, 647, (1985).

11. Yu, X., Nagarajan, M. R., Li, C., Speckhard, T. A., and Cooper, S. L., J. Appl. Polym. Sci., 30, 2135, (1985).

12. Somezawa, M., Ninomiya, Y., and Hashimoto, A., U. S. Pat., 4, 368, 238 (1983).

13. Schollenberger, C. S., and Dingbergs, K., J. Elast. and Plast., 5, 222, (1973).

14. Schollenberger, C. S., and Dingbergs, K., J. Elast. and Plast., 11, 58, (1978).

15. Speckhard, T. A., Ver Strate, G., Gibson, P. E., and Cooper, S. L., Polym. Engr. and Sci. 23, 337, (1983).

16. Van Bogart, J. W. C., Lilaonitkul, A., Lerner, L. E., and Cooper, S. L., J. Macromol. Sci. - Phys., 17, 267, (1980).

17. Van Bogart, J. W. C., Gibson, P. E., and Cooper, S. L., J. Polym. Sci., Polym. Phys. Ed., 21, 65, (1983).

18. Lilaonitkul, A., and Cooper, S. L., Advances in Urethane Science and Technology, 7, 163, (1979).

Table 1 Sample designation, chemical composition and molecular weight
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Sample	PTMA MW	Diisocyanate	Chain Extender	Molecular weight $\langle M_n \rangle$
ES1-57-G-M-U	996	MDI	glycerine	34,100
ES1-57-G-M-C	996	MDI	glycerine	-
ES1-69-G-I-U	996	IPDI	glycerine	57,900
ES1-69-G-I-C	996	IPDI	glycerine	-
ES2-73-G-M-U	2134	MDI	glycerine	31,900
ES2-73-G-M-C	2134	MDI	glycerine	-
ES4-84-G-M-U	4012	MDI	glycerine	45,500
ES4-84-G-M-C	4012	MDI	glycerine	-
ES4-84-D-M-U	4012	MDI	diaminohydroxyl propane	39,400
ES4-84-D-M-C	4012	MDI	diaminohydroxyl propane	-

Table 2 DSC Thermal Transition Data

SAMPLE	T_g °C	T_c °C	T_m °C	E_c Cal/g	E_m Cal/g	E_{mn} Cal/g soft seg.	
ES1-57-G-M-U	-11.3	--	--	--	--	--	--
ES1-57-G-M-C	-8.5	--	--	--	--	--	--
ES1-69-G-I-U	-33.4	--	--	--	--	--	--
ES1-69-G-I-C	-15.0	--	--	--	--	--	--
ES2-73-G-M-U	-28.1 -35.3*	--	53.5	--	9.63	13.23	--
ES2-73-G-M-C	-36.2 -36.1*	--	51.1	--	1.05	1.44	--
ES4-100	-52.4	--	55.2	--	20.99	20.99	--
ES4-84-G-M-U	-31.1 -40.4*	4.2	53.2 50.4	-7.17	10.04 8.86	11.92 10.52	
ES4-84-G-M-C	-41.7 -47.8*	-4.4	53.5 49.8	-6.54	8.39 7.12	9.96 8.45	
ES4-84-D-M-U	-37.1 -50.5*	-7.9	54.1 51.5	-6.43	11.48 11.28	13.79 13.38	
ES4-84-D-M-C	-41.3 -48.8*	-6.3	52.5 53.1	-5.99	10.62 9.09	12.64 10.78	

* Quenched Sample

T_g: Soft Segment Glass Transition Temperature
T_c: Soft Segment Crystallization Temperature
T_m: Soft Segment Melting Temperature
E_c: Energy of Crystallization
E_m: Energy of Fusion
E_{mn}: Energy of Fusion per gram of Soft Segment in the Material

Table 3   Tensile Properties
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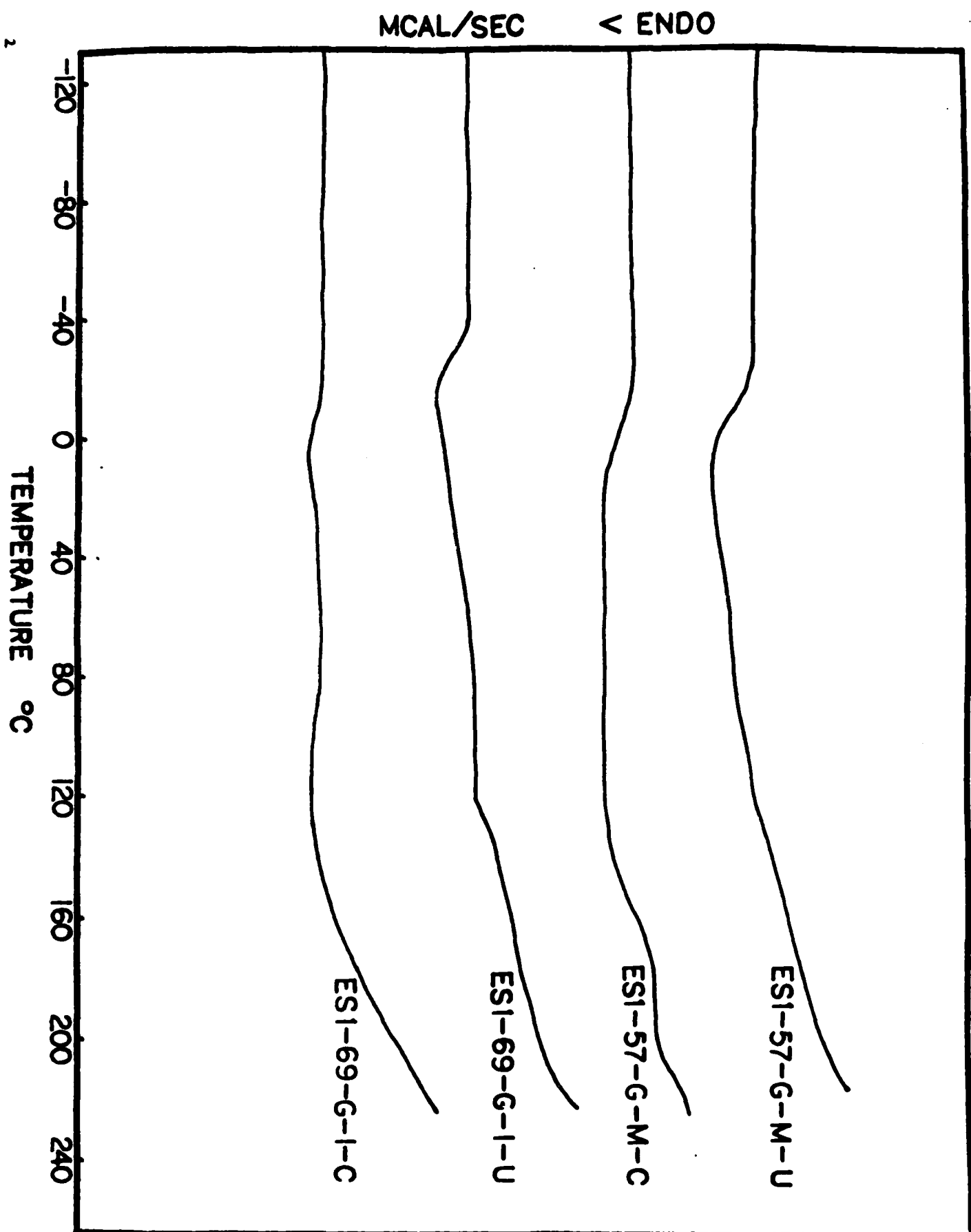| Sample	Young's modulus (Pa)	Ultimate stress (MPa)	Ultimate strain (%)
ES1-57-G-M-U	1.57E+08	8.04	552.8
ES1-57-G-M-C	7.40E+08	41.0	352.3
ES1-69-G-I-U	1.14E+08	7.33	612.9
ES1-69-G-I-C	4.55E+08	27.4	301.4
ES2-73-G-M-U	9.95E+08	11.9	740.7
ES2-73-G-M-C	1.08E+09	28.7	463.5
ES4-84-G-M-U	1.35E+09	15.4	470.2
ES4-84-G-M-C	1.36E+09	35.9	526.4
ES4-84-D-M-U	1.33E+09	14.8	749.2
ES4-84-D-M-C	2.28E+09	33.7	540.7

Figure Captions

Figure 1   DSC curves for the precursor and crosslinked materials with
different soft segment molecular weight (* designates quenched
samples).

Figure 2   DSC curves for the materials based on 1000 MW polyester soft
segments.

Figure 3   DSC curves for the materials based on 2000 MW polyester soft
segments (* designates quenched samples).

Figure 4   DSC curves for the materials based on 4000 MW polyester soft
segments (* designates quenched samples).

Figure 5   Dynamic mechanical spectra for materials based on the 1000 MW
polyester soft segments.

Figure 6   Dynamic mechanical spectra for crosslinked materials based on 1000,
2000, and 4000 MW polyester soft segments.

Figure 7   Dynamic mechanical spectra for materials based on the 4000 MW
polyester soft segments.

Figure 8   Stress-strain curves for precursor and crosslinked materials based
on 1000 and 2000 MW polyester soft segments.

Figure 9   Stress-strain curves for precursor and crosslinked materials based
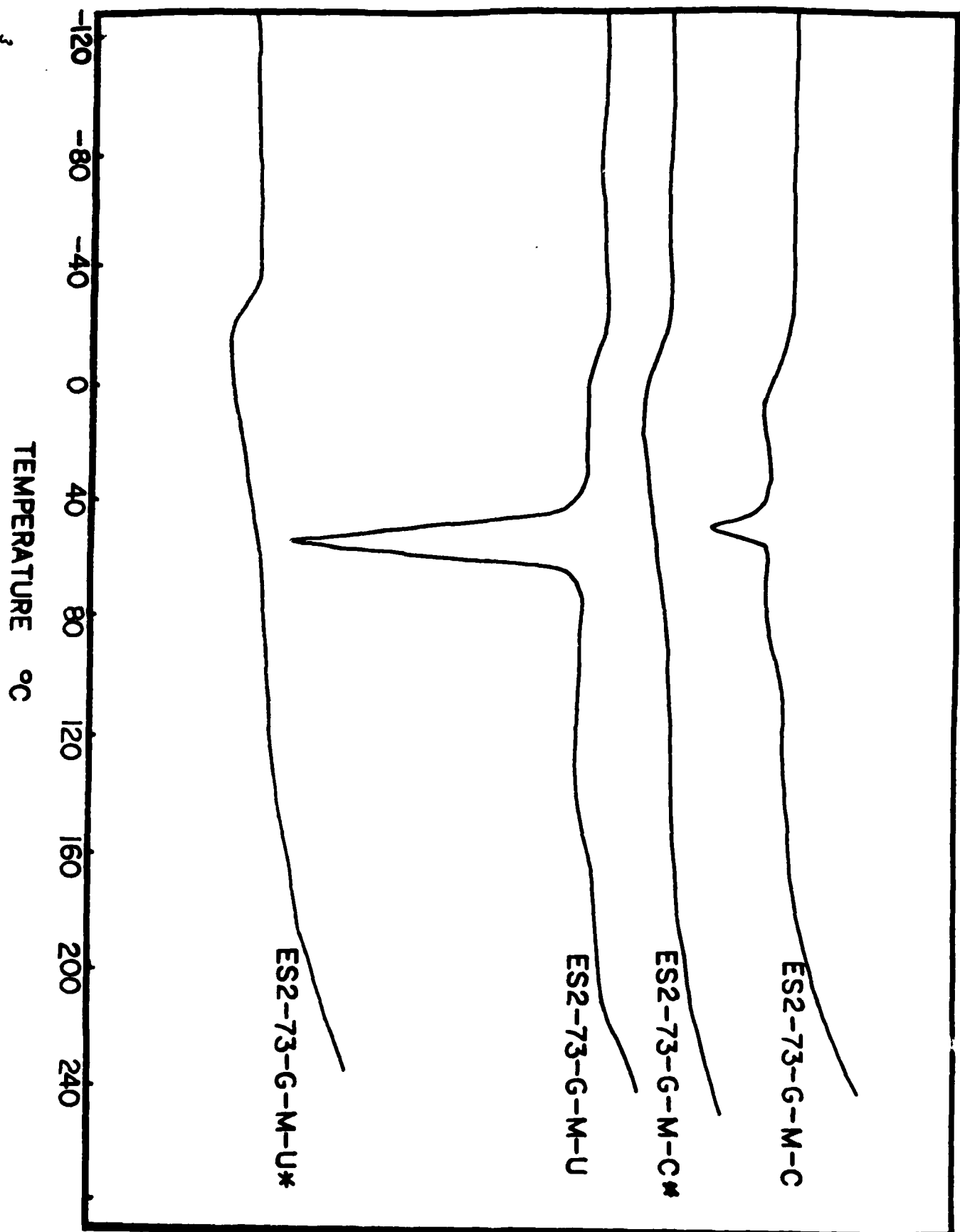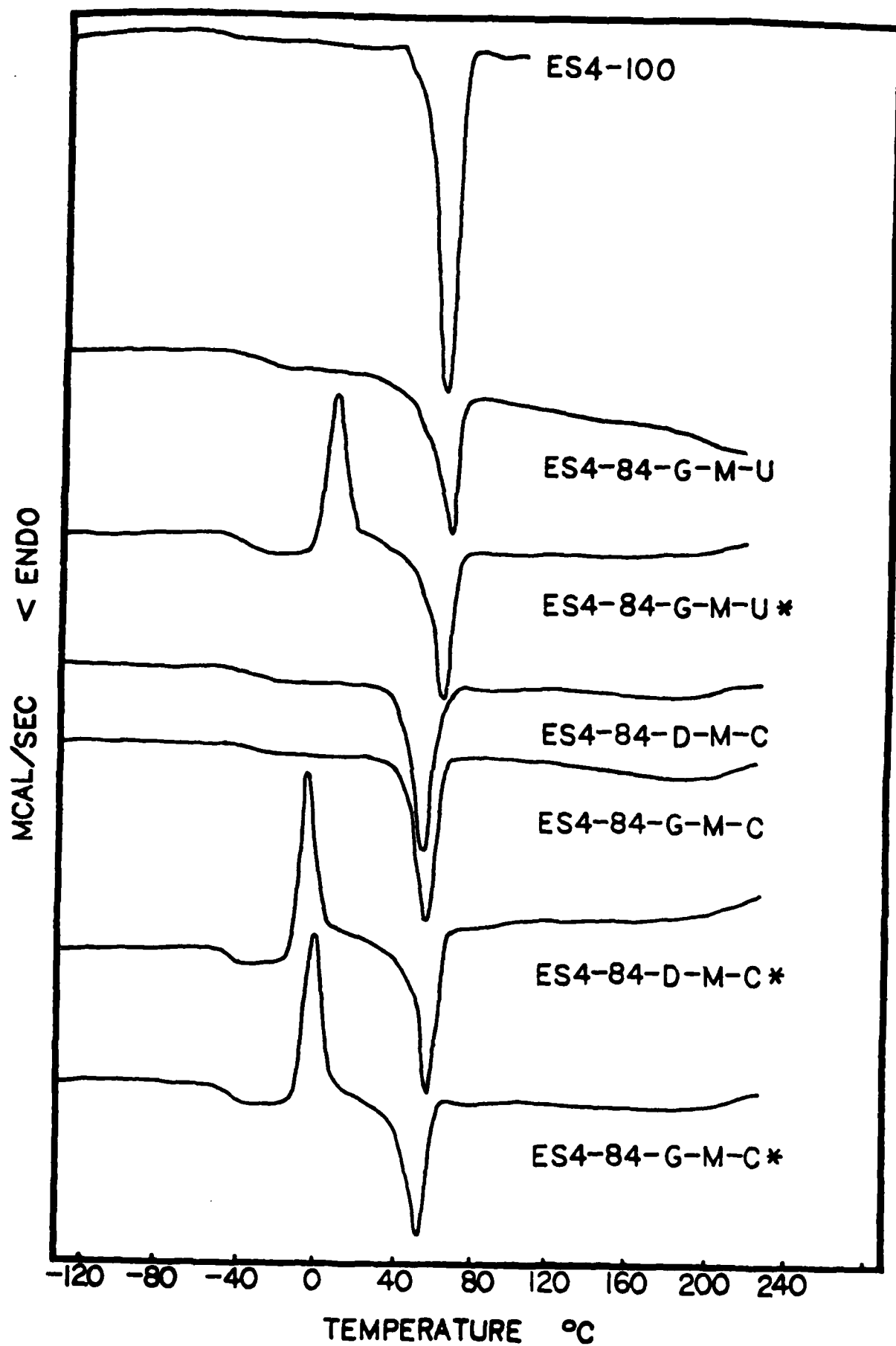on 4000 MW polyester soft segments.
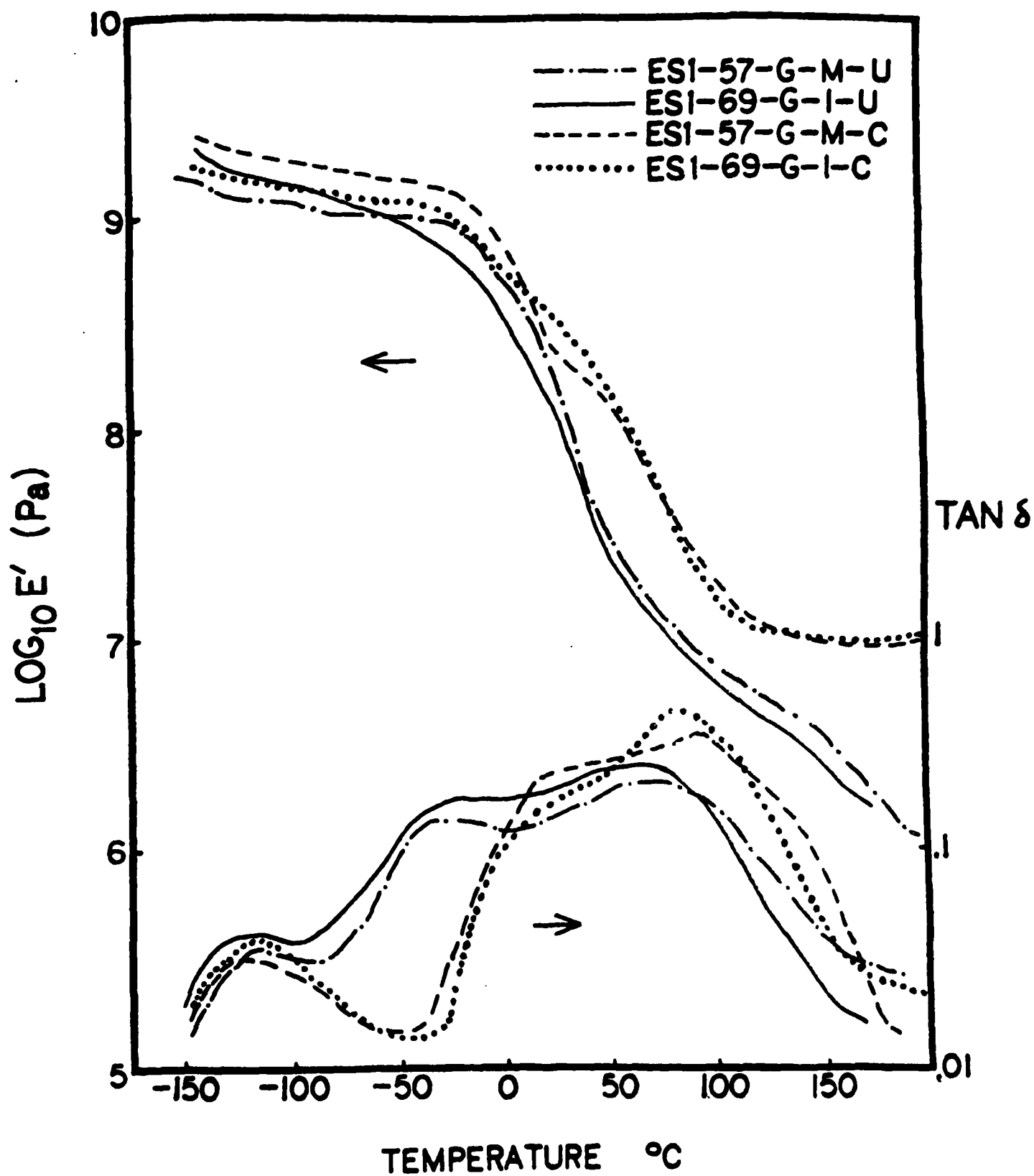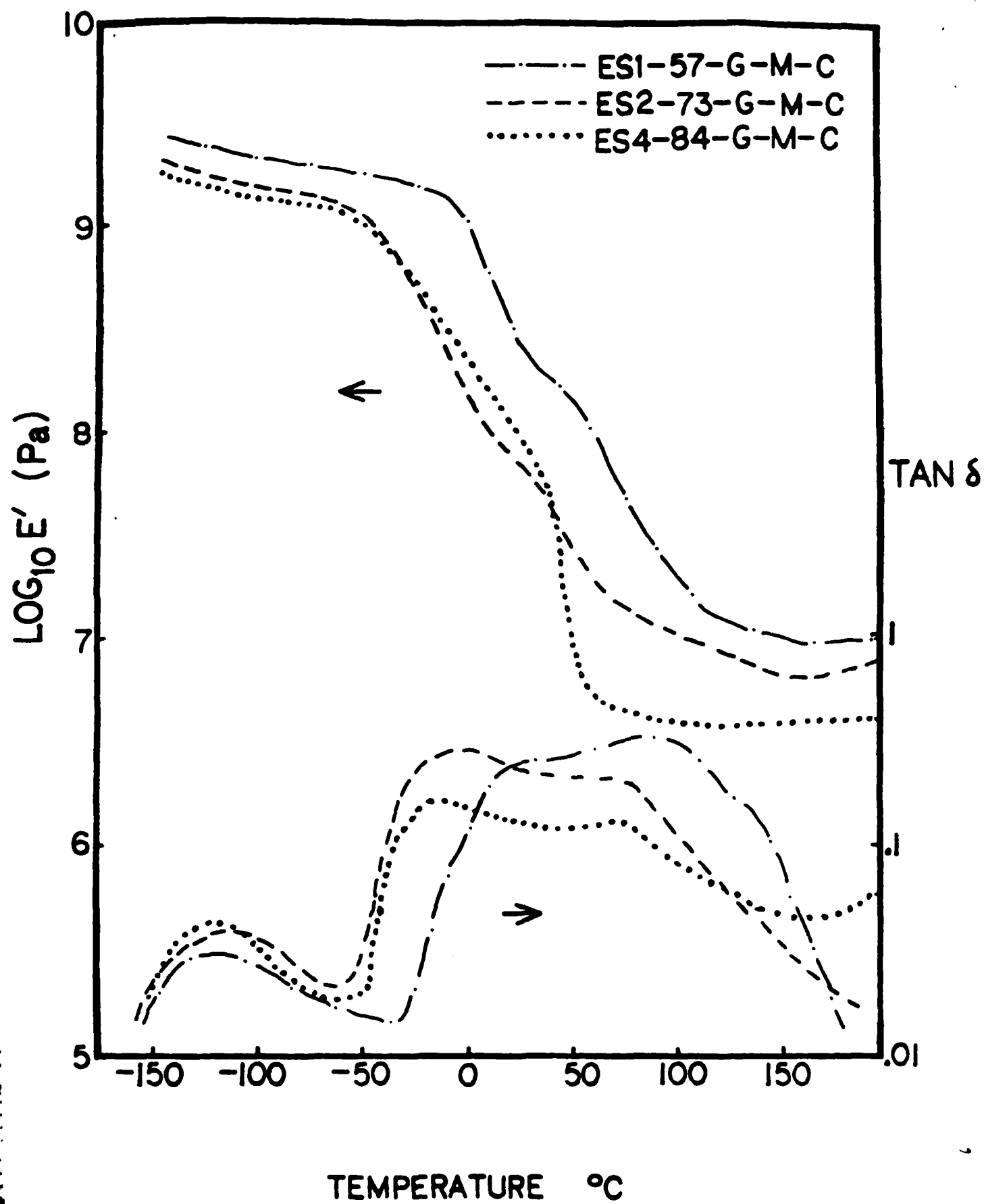
MCAL/SEC   < ENDO

TEMPERATURE °C

ES4-84-G-M-C*

ES4-84-G-M-C

ES2-73-G-M-C*

ES2-73-G-M-C

ES1-57-G-M-C*

ES1-57-G-M-C

MCAL/SEC   < ENDO

TEMPERATURE °C

-120 -80 -40 0 40 80 120 160 200 240

ESI-69-G-I-C

ESI-69-G-I-U

ESI-57-G-M-C

ESI-57-G-M-U

MCAL/SEC   < ENDO

MCAL/SEC   < ENDO

TEMPERATURE °C

-120   -80   -40   0   40   80   120   160   200   240

ES2-73-G-M-U*

ES2-73-G-M-U

ES2-73-G-M-C*

ES2-73-G-M-C

PSI

4000

3000

2000

1000

ELONGATION %

STRESS MPa

30

20

10

ES1-57-G-M-C

ES1-69-G-I-C

ES2-73-G-M-C

ES2-73-G-M-U

ES1-57-G-M-U

ES1-69-G-I-U

100   200   300   400   500   600

STRESS MPa

ELONGATION %

PSI

4000

3000

2000

1000

30

20

10

ES4-84-G-M-C

ES4-84-D-M-C

ES4-84-G-M-U

ES4-84-D-M-U

END

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